METHODS AND APPARATUS FOR DETERMINING OPTICAL CONSTANTS OF SEMICONDUCTORS AND DIELECTRICS WITH INTERBAND STATES

Technical Field

The present invention concerns a method of and apparatus for calculating at least one physical parameter of a film where the physical parameter is related to scattering caused by interband states. The relating is based upon a theoretical model including a quantum mechanical transition equation for transitions between a band and interband states. The equation contains parameters whose values for a given film are obtained from fitting measured data from an optical instrument such as a reflectometer and/or ellipsometer to the model. The model with fitted parameters enables calculation of the physical parameters. A value of one of the fitted parameters is proportional to the concentration of one interband state and, when calibrated against the magnitude of a variable of a process for introducing the interband state in the material, the parameter can be used for material engineering or monitored for process control. The invention is applicable, for example, to the manufacture of semiconductor or dielectric materials where alien species are introduced

into the material as microscopic impurities which induce interband states.

Background and Summary

Various schemes have been proposed for evaluating physical

5 parameters of a semiconductor. In one example disclosed in U.S. Patent

No. 4,854,710, information is derived by analyzing the interaction

between sample features and an electron-hole plasma induced in the

sample. Variations in plasma density, which is in part a function of

variations in the sample, are measured based on the effect of the plasma

10 on the refractive index at the surface of the sample. A radiation probe is

reflected off the surface of the sample and changes induced in the

refractive index are monitored to obtain information about surface and

subsurface characteristics of the sample.

The patentees in U.S. Patent No. 4,854,710 state that their

15 invention can be used for microscopically evaluating ion dopant

concentrations in a semiconductor by measuring changes in reflectivity of

a probe beam. A periodic energy beam is used to infuse energy into the

sample and create an electron-hole plasma. The diffusion profile or

changing density of the plasma is detected at the sample surface through

20 the use of the probe beam. The changing output signals of the detected,

reflected probe beam which are in phase with the energy beam can be

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plotted to indicate variations in dopant or defect concentrations. These output signals are compared to predetermined reflectivity measurements made on a known reference sample. The latter information can be stored in a processor and compared to give relative information concerning the tested sample.

U.S. Patent No. 5,883,518 discloses a doping level measuring system which may be used to control a semiconductor fabrication process. In the measuring system a detector detects the phase shift of an analyzer beam relative to a reference beam, and the doping level in a preselected doped region is determined from the phase shift. The phase shift of an analyzer beam is also detected in a method disclosed in U.S. Patent No. 5,966,019, which employs both an analyzer beam and a generation beam. A property of a semiconductor substrate is calculated from the detected phase shift.

U.S. Patent No. 6,049,220 discloses an apparatus and method for evaluating a wafer of semiconductor material which use diffusive modulation (without generating a wave of carriers) for measuring a material property (such as any one or more of mobility, doping, and lifetime) that is used in evaluating a semiconductor wafer. The measurements are based on measurement of reflectance, for example, as a function of carrier concentration. In one implementation, the

semiconductor wafer is illuminated with two beams, one with photon energy above the band gap energy of the semiconductor, and another with photon energy near or below the band gap. An attribute, derived from measurements on the wafer is interpolated with respect to corresponding attributes of wafers having a known material property (or process condition) to determine a corresponding property or condition of the wafer under measurement.

The Cauchy empirical model is the basis for modeling at least one physical parameter of a film for a wide variety of materials. Cauchy modeling can predict the experimental results in the long wavelength range where such optical transitions as band-to-band and band-to-interband state transitions do not occur. For example, Cauchy modeling can be used to fit the reflectance and ellipsometric measurement data of organic arc material for wavelengths longer than about 450 nm. However, data from measurements with light in the ultraviolet wavelength range do not match up well with the data predicted by the Cauchy model. There is a need for an improved model and method of calculating at least one parameter of a film using the model, which can accurately simulate or model the characteristic of a material for measurements over a wide range of wavelengths, including those in the ultraviolet wavelength range. An accurate model and method suitable for

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use with semiconductor materials and dielectrics having varying concentrations of interband states in the material would also be beneficial.

To this end, the improved method of the present invention for calculating at least one physical parameter of a film comprises relating at least one physical parameter to scattering caused by interband states. This relating includes using a theoretical model which includes a quantum mechanical transition equation for transitions between valence and/or conduction bands and interband states of the material. The method can be used for calculating the refractive index and the extinction coefficient of the film. It is applicable for semiconductor and dielectric film materials having varying levels of interband states. Apparatus for producing and monitoring films having at least one desired physical parameter, which employ the method are also provided.

These and other features and advantages of the present invention will become more apparent from the following description when taken in connection with the accompanying drawings which show, for purposes of illustration only, several example embodiments in accordance with the present invention.

Brief Description of Drawings

Figure 1 is a schematic illustration of an optical transition between valence band and an interband state, causing a detectable drop in reflectance.

Figure 2 is a graph showing the measured fitted results of reflectance of a film of organic anti-reflective coating (ARC) to incident light, wherein the three plots shown are one of measured data (shown by small circles) from the organic ARC material, a second plot (solid line) which is a simulation of the reflectance as a function of wavelength of the incident light for the same material from the model of the present invention, and a third plot (dashed line with cross hatching) which is a simulation based on the empirical Cauchy model.

Figure 3 is a schematic illustration of an embodiment of an apparatus for introducing or controlling interband states in a film according to a method of the present invention.

Figure 4 is a schematic illustration of another embodiment of an apparatus for monitoring films according to the present invention.

Figure 5 is a graph showing the measured fitted results of reflectance of a film of a polymeric low k dielectric material which has been cured at a temperature of 450°C for a curing time of 5 minutes, wherein the two plots shown are one of measured data (shown by small

circles) from the silicon material, and the second plot (solid line) is a

simulation of the reflectance as a function of wavelength of the incident

light for the same material from the model of the present invention.

Figure 6 is a graph showing the fitted parameter A of the model of

the invention as a function of the cure temperature, with a curing time of

5 minutes, for the film of polymeric low k dielectric material.

Figure 7 is a graph showing the fitted parameter A of the model of

the invention as a function of the cure time, with a cure temperature of

450°C, for the film of polymeric low k dielectric material.

Detailed Description

The disclosed example embodiment of the present invention is a

simulation method for calculating the refractive index n and the

extinction coefficient k for film materials containing varying levels or

concentrations of interband states. In the method, the physical parameters

n and k of a film which are calculated are related to scattering caused by

interband states. This is accomplished by modeling using a theoretical

model which includes a quantum mechanical transition equation for

transition between valence and/or conduction bands and interband states.

By way of explanation, it is known from equation (1) below from

electromagnetic theory that

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(1) $\varepsilon_2 = cn\alpha/\omega$, where

       ε_2 is the imaginary part of the dielectric function;

       c is the speed of light;

       n is the refractive index;

5   α is the absorption coefficient; and

       ω is the angular frequency of light.

For the case of semiconductor or dielectric materials with interband states, it is known from equation (2) below that:

(2) $\alpha = N_T\sigma$, where

10   N_T is the concentration of absorption centers per unit volume, such as per cm^3; and

       σ is the capture cross section of an absorption center.

The effect of interband states in a semiconductor or dielectric material on the optical properties, such as reflectance, of the material with varying wavelengths of incident light can be seen from the measured plot

15 depicted in Figure 2. The two sharp peaks in the reflectance, each followed by a sharp drop in reflectance, for light within the 2,000-2,500Å wavelength are believed to be caused by the presence of interband states. These peaks do not occur in semiconductor or dielectric materials where

20 interband states are absent.

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Transparent, dielectric films are known to exhibit strong absorption bands. When the wavelength of the incident light approaches an absorption band of the material from the long-wavelength side, the refractive index of the material becomes very large, then decreases within the band to assume abnormally small values on the short-wavelength side, values below those for radiation on the long-wavelength side. The expression "normal variation" is used to describe the change in the refractive index of a material with changing wavelengths of light for wavelengths far removed from those of the absorption bands of the material. This variation can be expressed by Cauchy's formula. The expression "anomalous variation" refers to the very large increase and then decrease of the refractive index, or reflectance as shown in Figure 2, as the wavelength approaches the absorption band from the long-wavelength side, then decreases within the band to assume abnormally small values on the short-wavelength side.

The method of the present invention is explained with reference to the schematic illustration in Figure 1, wherein the band gap, close to 10 eV, for example, between the valence band and the conduction band is relatively large, higher than the energy level of the incident photons of the light used for the measurements of the material over the wavelength range shown in Figure 2. To explain the anomalous variations, e.g., the

sharp peaking and then decrease of the reflectance in the wavelength

range 2,000-2,200 Å and the wavelength range 2,300-2,450 Å as shown

in Figure 2, interband states in the material which absorb energy in these

wavelength ranges are considered to account for these abrupt changes.

5   That is, the presence of the interband states permits absorption of energy

by transition of electrons from the valence or conduction band to the

interband state level, E_D.

A general quantum mechanical transition equation appears in

equation (3) below. See J. Tauc et al.: "Optical Properties and Electronic

10   Structure of Amorphous Germanium, *Phys. Stat. Sol.* 15, 627 (1966) at

page 634.

(3) $$\varepsilon_2(\omega) = \left(\frac{2\pi e}{m\omega}\right)^2 \frac{1}{V} \sum_{i,f} \left|P_{if}\right|^2 \delta(E_f - E_i - E), \text{where}$$

15   $\varepsilon_2(\omega)$ is the imaginary part of the dielectric function;

P_{if} is the momentum matrix element between the wave functions of

the final and initial states;

E_f is the energy level of the final state;

E_i is the energy level of the initial state;

20   E is the incident photon energy;

V is the volume;

m is electron mass; and

ω is the angular frequency of light.

Transition between an interband state and band, is described by the

following derived equation (4). See J. Bourgoin et al.: *Point Defects in*

Semiconductors II Experimental Aspects, Springer-Verlag Berlin

Heidelberg New York 1983, page 110.

$$(4) \qquad \varepsilon_2(\omega) = \begin{cases} A\dfrac{\sqrt{E - E_D}}{E^2}, & \text{for } E > E_D \\ 0, & \text{for } E < E_D \end{cases}$$

where A and E_D are parameters which can be determined from

fitting measured data from a film according to the model.

From the Kramer Konig relation, $\varepsilon_1(\omega)$ can be calculated from ε_2

according equation (5) as follows.

$$\varepsilon_1(\omega) = \varepsilon_1(\infty) + \frac{2}{\pi} \wp \int_0^\infty \frac{x\varepsilon_2}{x^2 - E^2}\, dx$$

(5)

$$= \begin{cases} \varepsilon_1(\infty) + A\dfrac{2\sqrt{E_D} - \sqrt{E_D + E} - \sqrt{E_D - E}}{E^2}, & \text{for } E < E_D \\ \varepsilon_1(\infty) + A\dfrac{2\sqrt{E_D} - \sqrt{E_D + E}}{E^2}, & \text{for } E > E_D \end{cases}$$

where $\qquad \varepsilon_1(\omega)$ is the real part of the dielectric function; and

$\varepsilon_1(\infty)$ is the value of $\varepsilon_1(\omega)$ at infinite angular

frequency. This is a fitted parameter for the material obtained from measured data.

According to the invention, the parameters for fitting ellipsometric and reflectivity data using the model of the invention are thickness, $\varepsilon_1(\infty)$, and two additional parameters per defect level (A and E_D). Therefore, the maximum number of parameters will be 2 + 2 times the number of interband state levels present. Solving for the fitting parameters from measurements from a given material allows one to calculate ε_1 and ε_2 from which n and k can be calculated according to the following relations (6) and (7):

$$(6) \quad n = \sqrt{\frac{1}{2}\left[\sqrt{\left(\frac{\varepsilon_1}{\varepsilon_2}\right)^2 + \left(\frac{\varepsilon_2}{\varepsilon_0}\right)^2} + \frac{\varepsilon_2}{\varepsilon_0}\right]}$$

$$(7) \quad k = \sqrt{\frac{1}{2}\left[\sqrt{\left(\frac{\varepsilon_1}{\varepsilon_0}\right)^2 + \left(\frac{\varepsilon_2}{\varepsilon_0}\right)^2} + \frac{\varepsilon_1}{\varepsilon_0}\right]}$$

The fitted parameter A in the above equations depends on the concentration of the interband state as it is implemented in equation (2). In a thin film semiconductor and dielectric manufacturing facility or FAB environment, the concentration of interband state is controlled by, for example, adjusting the concentration of alien species introduced into a

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host material or by adjusting film preparation conditions. For example, alien species will be introduced in gas phase in a reactive chamber and the amount of gas flow is the controllable variable. Thus, according to the invention, the parameter A can be monitored, either during or after a process for introducing alien species into the material, to monitor whether there is a problem of controlling the concentration of alien species being used in the production process.

More generally, the application of the method and model of the invention enable material engineering by calibrating the concentration of alien species against the fitted parameter A, calculating refractive index and extinction coefficient (n and k) for the corresponding A, and deciding the concentration of alien species for the desired refractive index n and extinction coefficient k. Process control can be achieved by monitoring the fitted parameter A to monitor whether there is a problem of controlling the concentration of alien species, as noted above. An estimation of alien species in a film can also be obtained from the fitted parameter A.

The simulated plot in Figure 2, obtained using the measured data from an organic ARC film and the model of the invention, validates the theoretical model of the present invention in closely following the measured data for reflectance as a function of the wavelength of the

incident light. The other plot in Figure 2 was obtained from the empirical

Cauchy formula. As seen in Figure 2, the plot from the Cauchy formula

is not accurate in the wavelength range illustrated in Figure 2 because it

does not account for changes due to the presence of interband states in the

5   material.

An apparatus 1 depicted in Figure 3 according to the invention for

producing a film having at least one desired physical parameter comprises

a processing device 2 for introducing or controlling interband states in a

film which affect the optical dispersion of the film. For example, an

10   impurity can be carried by gas for diffusion into a material in the device 2

as will be understood by the skilled artisan. Other process variables

which could be controlled include the temperature and/or time of

treatment of the film being processed. An optical instrument 3, such as a

reflectometer or ellipsometer, is provided for producing measured data

15   from a film, either *in situ* in the device 2 during process or after

production of the film with interband states.

A controller 4 of the apparatus adjusts a concentration of alien

species being introduced in a film by the processing device 2 or adjusts

another process variable, such as time and/or temperature of a treatment

20   performed by the processing device causing interband states.

Illustratively, the amount of gas flow containing the alien species to be

introduced into a material can be adjusted by the controller for obtaining

a material having the desired properties. The controller 4 receives

measured data from the optical instrument 3. The controller can be a

programmed processor such as a microprocessor that calculates a

5   physical parameter or parameters of the measured film using the

measured data and the theoretical model of the invention relating the

physical parameter to scattering caused by film interband states in the

material as discussed above.

An apparatus 6 of the invention depicted in Figure 4 comprises an

10   optical instrument 7 for measuring a film in which an alien species has

been introduced or a film otherwise treated to have varying

concentrations of interband states and for producing measured data as a

result of the film measuring. The device 7 can be a reflectometer and/or

ellipsometer, for example. A programmed processor 8 calculates at least

15   one physical parameter of the measured film and displays it at display 9

using the measured data and the theoretical model according to the

invention relating the physical parameter to scattering caused by

interband states in the film. From initial measured data of a sample, the

fitting parameters of the model can be calculated for use in calculating n

20   and k and the fitted parameter A can be monitored for the aforesaid

purposes.

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Figure 5 shows the measured fitted results according to the present

invention of reflectance of a film of a polymeric low k dielectric material

by Dow Chemical Company. The film was processed by a process which

caused varying concentrations of interband states. The concentration or

5   level of interband states in the processed film was, at least in part, a

function of both a curing temperature and also a cure time of the process.

The two plots shown in Figure 5 are each reflectance as a function of

wavelength of the incident light on the material, one from measured data

(shown by small circles) from the polymeric low k dielectric material,

10   and the second plot (solid line) from a simulation from the model of the

present invention. The measured fitted results in Figure 5 are for film

cured at a temperature of 450°C for a cure time of 5 minutes. The

simulated plot in Figure 5 is seen to closely follow the measured data,

further validating the model of the invention.

15   Figures 6 and 7 are graphs of the fitted parameter A of the model of

the present invention as a function of the cure temperature, Figure 6, with

a cure time of 5 minutes, for the film of polymeric low k dielectric

material, and as a function of the cure time, Figure 7, with a cure

temperature of 450°C, for the film. Values for the fitted parameter A as a

20   function of cure temperature and cure time for the film material having

three levels of interband states, A1, A2 and A3, are shown in Table I

below. The values for the fitted parameter A for the material with concentration A2 of interband states are shown as a function of cure temperature and cure time in Figures 6 and 7, respectively.

TABLE I

Cure Temperature (°C)	Cure time (minutes)	Al	A2	A3
430	5	19.97	3.317	0.802
560	3	18.37	4.398	1.051
450	5	19.09	3.806	0.944
450	7	17.76	4.690	1.124
470	5	16.49	5.674	1.312

While I have shown and described only several embodiments in accordance with the present invention, it is understood that the same is not limited thereto, but is susceptible to numerous changes and modifications as known to those skilled in the art. For example, although the method and apparatus of the invention have been explained in connection with calculating physical parameters, and material engineering, of materials where interband states are caused by introduction of alien species into the material, the method and apparatus are useful with materials and in processes wherein interband states are

caused by other mechanisms, such as by dislocations or coordination,

e.g., bonding defects in the material. Therefore, I do not wish to be

limited to the details shown and described herein, but intend to cover all

such changes and modifications as are encompassed by the scope of the

5   appended claims.